

NOTE

Non-Covalent Immobilization of C₆₀ in Benzoic Acid Modified Layered Double Hydroxides

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Fullerene was non-covalently immobilized in the interlayer of benzoic acid modified layered double hydroxides and the supramolecular structure. The physico-chemical behaviour were characterized by XRD and UV-VIS.

Key Words: Fullerene, Layered double hydroxides, Benzoic acid.

Fullerene (C₆₀) possesses many attractive and potentially useful physical and chemical properties¹. Moreover, fullerenes and their derivatives have been shown to be promising favourable magnetic, superconductivity, electrical, nonlinear optics, ion-selective electrode, single-molecule devices and organic memory devices²⁻⁵. Drawbacks for their use in several applications, especially those based on optical and electronic properties, arise from their difficult processibility and incorporation into various solid matrixes such as polymers, glasses, metals and other materials⁶⁻⁸.

Layered double hydroxides (LDHs) are unusual layered materials consisting of positively charged layers with charge balancing anions between the sheets. Layered double hydroxides can be represented by the formula [M²⁺_{1-x}M³⁺_x(OH)₂]^{x+}(Aⁿ⁻_{x/n})·mH₂O (M²⁺ divalent and M³⁺ trivalent metals, respectively, Aⁿ⁻ n-valent anion)^{9,10}. They have recently received increasing attention, owing to their versatility and usefulness in a wide range of technological applications such as functional materials¹¹, adsorbents¹², two dimensional solid-state nano-reactors¹³, bioactive nanocomposites¹⁴, and so on. Incorporation of C₆₀ into layered double hydroxides is intriguing because the C₆₀ molecules can be arranged in two-dimensional arrays. The resultant sandwiched C₆₀ is expected to have physico-chemical properties in between those of the free molecules and the molecules trapped in the one-dimensional tunneling matrix⁷.

In this work, the precursor NO₃-LDHs was prepared by a coprecipitation method similar to that reported previously¹⁵. The benzoic acid (BA) intercalated layered double hydroxides (BA-LDHs) was obtained by the method of ion exchange. In a typical intercalation of C₆₀ into layered double hydroxides experiment, powdered BA-LDHs was added into xylene

solution of C₆₀ and then the mixture was stirred for 48 h at 70 °C with ultrasonic treatment. The colour of the powder changed from white to brown or dark brown. The powder was filtered and washed with toluene to remove excess C₆₀ until the filtrate was colourless. This sample is denoted as C₆₀/BA-LDHs.

The powder XRD patterns of NO₃-LDHs, BA-LDHs and C₆₀/BA-LDHs are displayed in Fig. 1. All the three patterns indicate formation of well-crystallized hydroxalite-like phase. In each case, the reflections can be indexed to a hexagonal lattice with R-3m rhombohedral symmetry, commonly used for the description of layered double hydroxides structures. The intercalation of benzoic acid inside the lamellar host structure was clearly confirmed by the net increase of the basal spacing d₀₀₃ from 0.884 nm for the precursor NO₃-LDHs to 1.623 nm for BA-LDHs. Taking into account the dimensions of the benzoic acid molecule, it possibly adopts a monolayer arrangement with its molecules perpendicular to the layered double hydroxides sheets. Furthermore, It was found that, upon inclusion of C₆₀ (Fig. 1c), the value of d₀₀₃ of C₆₀/BA-LDHs increased from 1.623 to 1.759, corresponding to increases of 0.136 nm, which indicating the C₆₀ molecules has been successfully included into the interlayer of LDHs. Moreover, the increase in the FWHM value of the (003) line from BA-LDHs to C₆₀/BA-LDHs demonstrates that the crystallinity of the LDHs phase decreases upon incorporation of C₆₀ with ultrasonic treatment. A schematic representation of the possible arrangement for C₆₀/BA-LDHs is shown in Fig. 2.

The chemical compositions of the synthesized powder products NO₃-LDHs, BA-LDHs and C₆₀/BA-LDHs are listed in Table-1. As shown in Table-1, the experimentally determined Zn/Al molar ratio of BA-LDHs is approximately equal to that

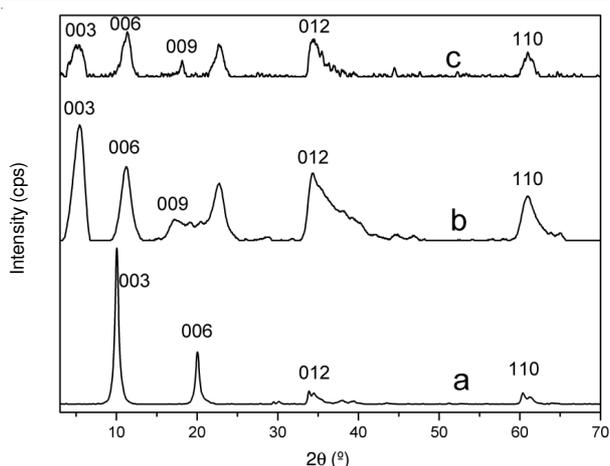


Fig. 1. Powder XRD patterns of (a) NO_3 -LDHs, (b) BA-LDHs, (c) C_{60} /BA-LDHs

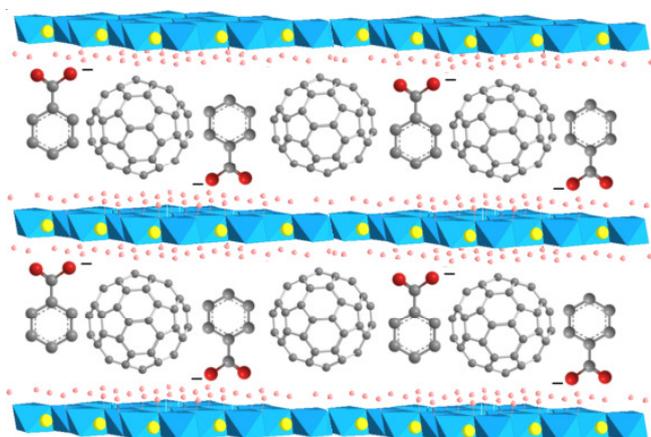


Fig. 2. Schematic representation of the possible arrangement of C_{60} /BA-LDHs

TABLE-1
CHEMICAL COMPOSITIONS FOR
 NO_3 -LDHs, BA-LDHs, C_{60} /BA-LDHs

Sample	Chemical composition
NO_3 -LDHs	$\text{Zn}_{0.66}\text{Al}_{0.34}(\text{OH})_{2.00}(\text{NO}_3)_{0.34} \cdot 0.8\text{H}_2\text{O}$
BA-LDHs	$\text{Zn}_{0.66}\text{Al}_{0.34}(\text{OH})_{2.00}(\text{BA})_{0.319}(\text{NO}_3)_{0.021} \cdot 2.2\text{H}_2\text{O}$
C_{60} /BA-LDHs	$\text{Zn}_{0.65}\text{Al}_{0.35}(\text{OH})_{2.00}(\text{BA})_{0.33}(\text{C}_{60})_{0.021}(\text{NO}_3)_{0.020} \cdot 1.5\text{H}_2\text{O}$

of the NO_3 -LDHs precursor and it decreased slightly after the inclusion of C_{60} into the BA-functionalized LDHs. The extent of inclusion of C_{60} in the BA-LDHs was found to correspond to a ratio of 0.07 molecules of C_{60} per benzoic acid molecule.

Fig. 3 shows the UV-visible spectra of C_{60} -containing LDHs as well as the corresponding reference samples. It was found that the spectrum of solid C_{60} powder displays broad bands appearing at 316 nm, in accord with the literature⁷. Furthermore, it was found that the absorption bands of C_{60} /BA-LDHs centered at 309 nm which is a significant blue shift compared with that of C_{60} powder (316 nm). Most probably, the shift to shorter wavelength is reminiscent to the restrict effect by the layered double hydroxides sheets. This confinement imposes stronger restriction on the rotation and translation of the guest molecule, as well as the increased interactions between guest and host. Therefore, an obvious blue shift in emission spectrum for C_{60} /BA-layered double hydroxides can be detected.

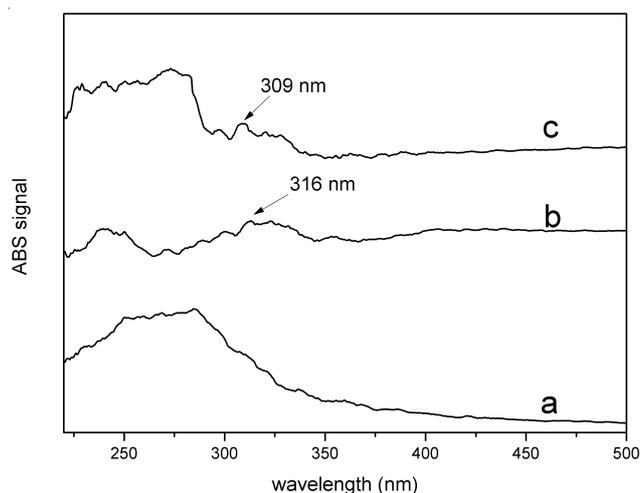


Fig. 3. UV-VIS spectra of (a) BA-LDHs, (b) C_{60} powder, (c) C_{60} /BA-LDHs

Conclusion

This study achieves the noncovalent immobilization of C_{60} in the interlayer of benzoic acid modified layered double hydroxides, taking advantage of the host-guest interaction between C_{60} , benzoic acid and layered double hydroxides. It can be expected that this fullerene-trapped layered double hydroxides materials may have potential application in the field of photoelectron-chemistry and optical limiting equipment.

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